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W432

REACTIONS OF COUMALINIC ACID AND PREPARATION OF ITS CHLORIDE

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

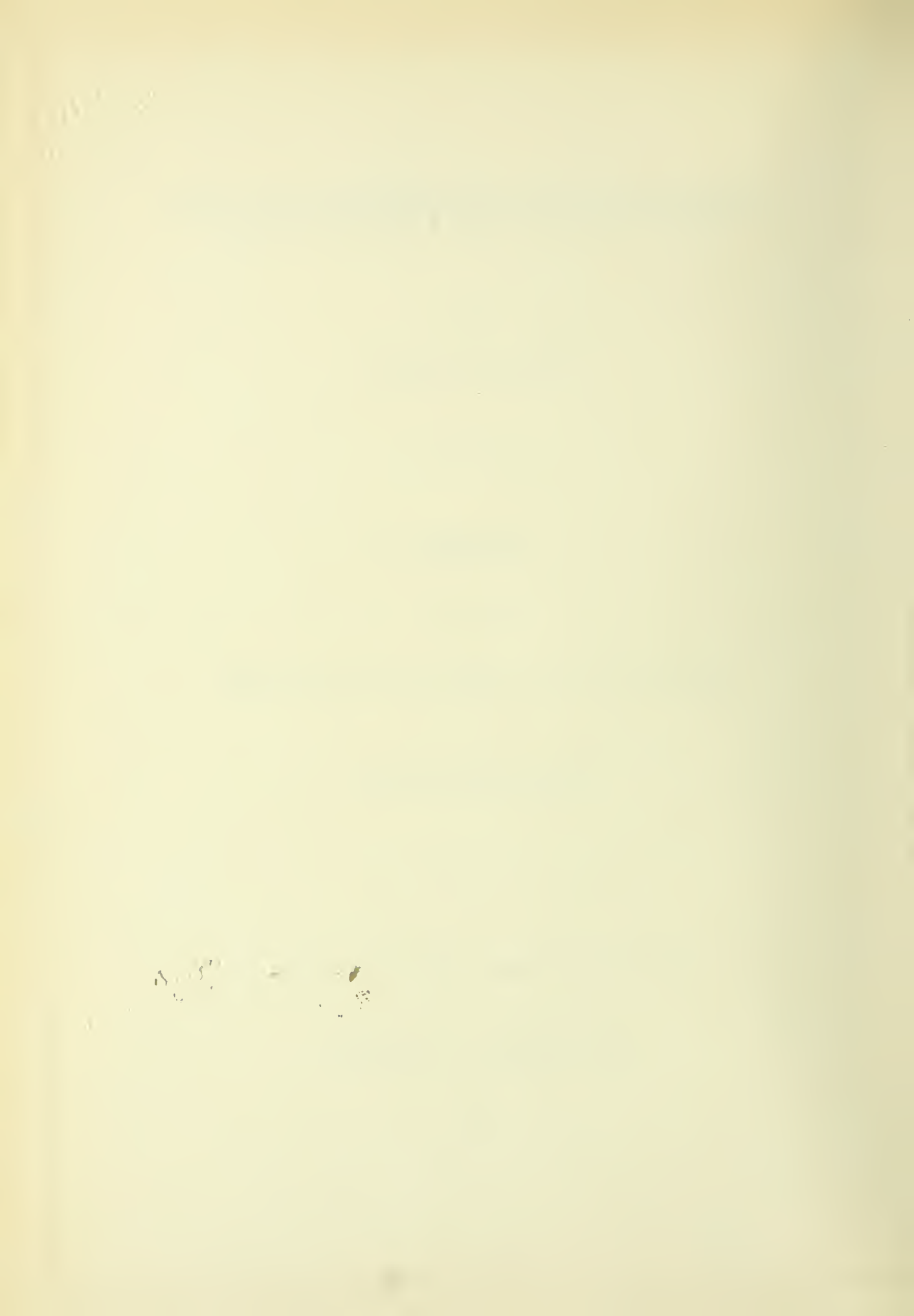
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CHEMICAL ENGINEERING

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1922



W432

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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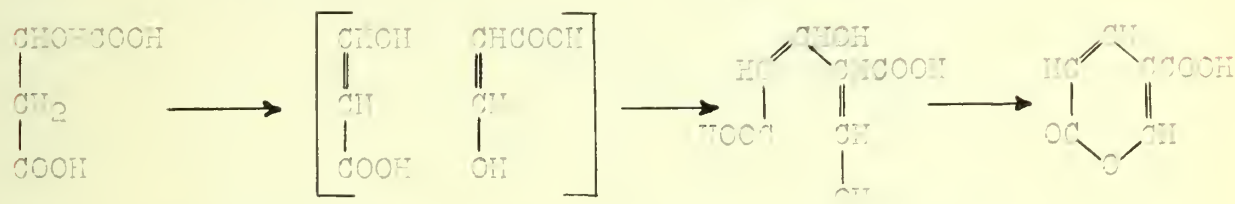
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HISTORICAL

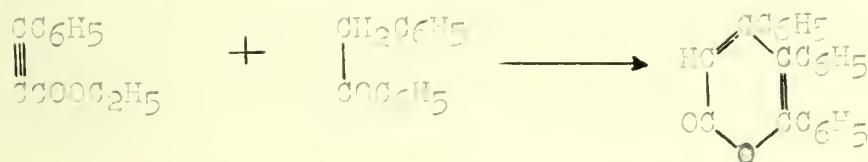
Alpha Pyrones

Alpha pyrones have been prepared by several general methods. First, by the action of concentrated sulphuric acid on an aldehydic acid or a ketonic acid. For example, coumalinic acid (I) was prepared in the following manner:

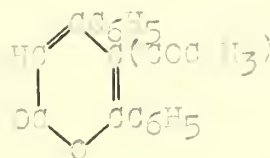
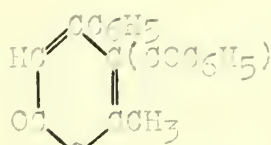


From acetacetin acid, isodehydracetic acid (IV) was obtained and in a similar manner acetodedicarboxylic acid gave citra-coumalinic acid (III).

Second, by the addition of β -ketonic esters and certain ketones to esters of acetylenic acids. Deoxybenzoin added to ethyl phenylpropiolate giving 4:5:6 triphenyl alpha pyrone (XV).

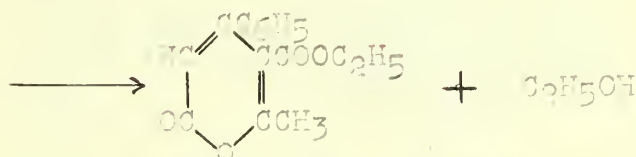
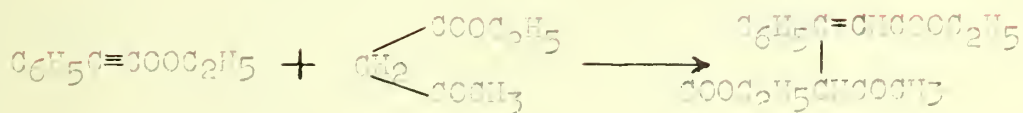


Acetylacetone and benzoylacetone in like manner gave respectively 4-phenyl-6-methyl-5-aceto alpha pyrone (XVI) and 4-phenyl-5-benzoyl-6-methyl alpha pyrone (XVII) or 4:6 di-phenyl-5-acetyl alpha pyrone (XVIII). In the latter case the formula of the compound is one of the following:



* See table for references.

The following equation expresses the reaction between ethyl acetoacetate and ethyl phenylpropiolate.



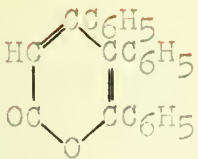
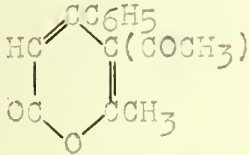
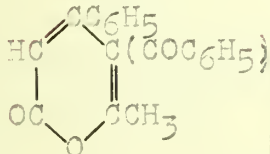
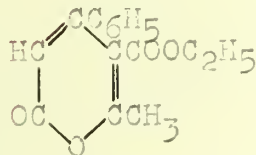
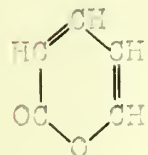
Ethyl-4-phenyl-6-ethyl alpha pyrone 5-carboxylate (XVIII).

The halogen derivatives of the alpha pyrone compounds were obtained by direct chlorination or bromination of the acids and esters. In some instances, as for example, in carrying out the chlorination of methyl coumalate, solvents were used such as carbon tetrachloride saturated with chlorine.

Coumalin (XIX) the simplest of the alpha pyrones was prepared by H.v. Pechmann by the dry distillation of mercurous coumalinate in an atmosphere of hydrogen.

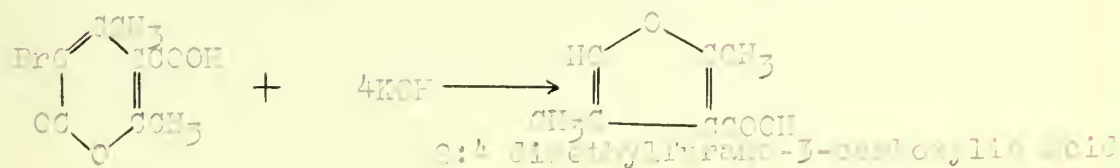
I		M.P. 205-210	Soluble in methyl alcohol, acetic acid, ether, water and acetone.	Ber. 17, 2334
II		M.P. 227-228	Soluble in alcohol, acetic acid, water, and acetone.	J.C.S. 1901 T.Pt. 2, 1280
III		M.P. 185 Turns dark at 150	Soluble in water and alcohol.	Annalen 261 190-202
IV		M.P. 50		Annalen 261 190-202
V		M.P. 74 B.P. 60 178-8	Soluble in ether, alcohol, acetone and water.	Annalen 264 271
VI		M.P. 36 B.P. 262-265	Soluble in ether, alcohol, acetone and water.	Annalen 264 261-309
VII		M.P. 59-60	Soluble in water, and in most organic media.	J.C.S. 1901 T.Pt. 2 1280

VIII		M.P. 127-129	Soluble in acetic acid, alcohol and ether.	Ber. 37, 3829-36
IX		M.P. 134-136	Soluble in chloroform, acetone, acetic acid, and benzol.	Ber. 17, 2396-2399
X		M.P. 176	Soluble in ether, alcohol, chloroform and glacial acetic acid	Ber. 17, 2396-2399
XI		M.P. 161-162	Soluble in alcohol and benzene.	Ber. 26, 746-747
XII		M.P. 72		Ber. 35, 782-790
XIII		M.P. 94-95	Soluble in alcohol	Annalen 321 367-384
XIV		M.P. 66-68	Soluble in ether, alcohol, acetic acid and water.	Ber. 27, 841-850

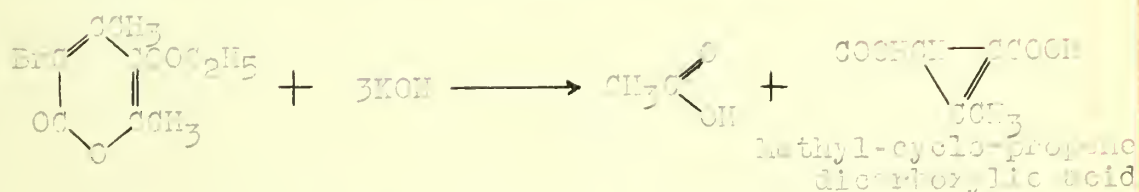
XV		M.P. 245-246	Soluble in glacial acetic acid. Insoluble in water or alcohol.	J.C.S. 1910 T. 457.
XVI		M.P. 128		J.C.S. 1899, T. 411.
XVII		M.P. 143-144		J.C.S. 1899, T. 411
XVIII		M.P. 104		Ber. 35, 782-795
XIX		B.P. 206-9d M.P. 5 B.P. 30 120	Miscible with all ordinary solvents.	Annalen 264 261-305

THEORETICAL

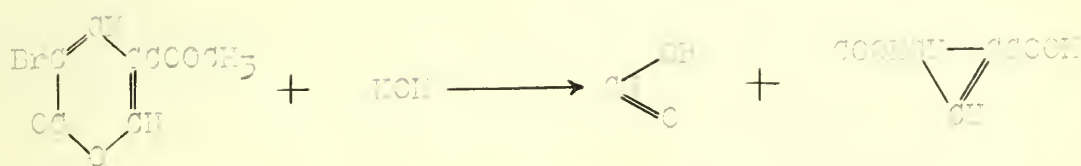
Trans Feist treated bromo-isodienhydracetic acid with potassium hydroxide and obtained a furane derivative.



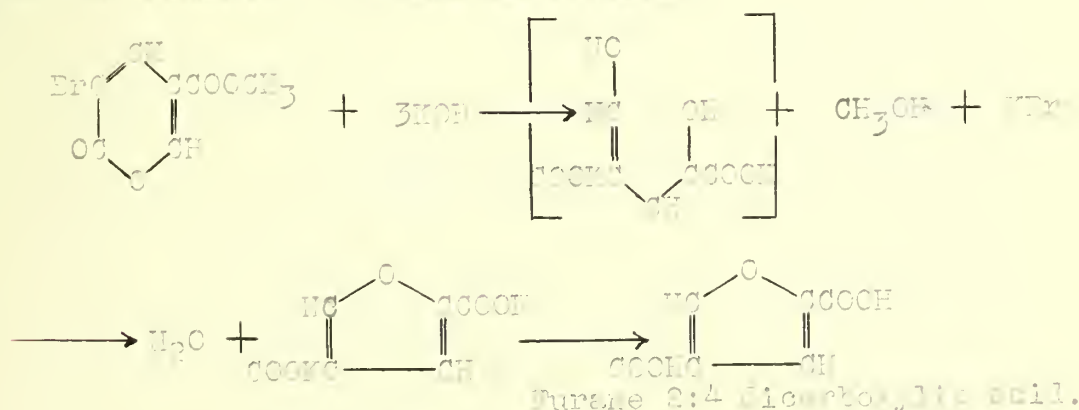
He then treated ethyl-bromo-isodienhydracetic ester with potassium hydroxide and obtained a cyclo propene derivative.



This led him to investigate a simpler alpha pyrone, methyl-bromo-cumalinate expecting to obtain a cyclo-propene compound similar to that obtained from the ethyl-bromo-isodienhydracetic ester.



Instead he obtained a furane derivative.



Since methyl-chloro-cumalinate (IX) prepared by

v. Pahlmeyer and Mills, was never converted either into the cyclo-propene derivative nor into the furane derivative. There existed a curiosity as to which of the two derivatives it would give on treatment with potassium hydroxide, which therefore led to this investigation.

EXPERIMENTAL

Conmalinic acid:-W.v.Pechmann prepared coumalinic acid (I) by heating malic acid (50 grams) in the water bath with a mixture of (75 grams) concentrated sulphuric acid and (75 grams) fuming sulphuric acid containing 10-12 per cent sulphur trioxide. When the evolution of carbon dioxide ceased in 1 1/2-2 hours, the solution was carefully mixed with ice (200 grams) and kept over night. The precipitated acid was separated by filtration, washed with ice water until almost free from sulphuric acid and then dried on porous plates. The acid in the mother liquors and washings was extracted by shaking six times with ether. The total yield of the crude product was about 30 per cent, but it contained fumaric acid and traces of trimesic acid. It was purified by dissolving in water between 70-80 degrees, shaking the solution with animal charcoal, and then extracting the acid with ether. It crystallized from from methyl alcohol and glacial acetic acid in colorless prisms, and on heating turned red at 200 degrees, and melted between 205-210 degrees with decomposition. It boiled at 213 degrees under a pressure of 100 mm. with partial decomposition.

As fuming sulphuric acid containing 10-12 per cent sulphur trioxide could not be obtained in the laboratory, fuming sulphuric acid containing 7 per cent sulphur trioxide was used and the amount per 50 grams of malic acid was calculated. A mixture of (40 grams) concentrated sulphuric acid and (110 grams) of fuming sulphuric acid 7 per cent sulphur

trioxide was used, and procedure as given by v. Tschernig was carried out. An 83 per cent yield of crude product was obtained but could not be purified according to v. Tschernig's method. Different methods of purification, and such solvents as alcohol, chloroform, acetone, ether, petroleum ether and ethyl acetate were tried but colorless prisms could not be obtained.

By dissolving the crude acid in hot glacial acetic acid and allowing it to cool the coumalic acid crystallized. The crystals had a yellowish color, and no definite shape. The yield of pure acid was 63 per cent.

Methyl Coumalinate.

Methyl coumalinate (V) was prepared by W.V. Peckmann by adding to one part of the acid 2 parts of sulphuric acid and heating for 15 minutes. Then adding one part of methyl alcohol and refluxing for one hour on a water bath. After cooling it was poured into water and filtered to remove ferric water and trisaccharate. The filtrate was extracted 12 times with ether, dried, the solution evaporated and the remaining substance crystallized in long needles. It was recrystallized from hot water, ether or ligroin. The yield was 75 to 85 percent of the weight of acid used, and the melting point was from 73-74 degrees.

Four methods of preparing the ester were tried.

- (1) The method used by W.V. Peckmann;
- (2) By passing dry hydrogen chloride into a mixture of acid and methyl alcohol;
- (3) By treating the silver salt of the acid with methyl iodide;
- (4) By passing methyl alcohol vapors through a mixture of acid, sulphuric acid and methyl alcohol.

(1) After following W. Peckmann's method of preparation, methyl coumalinate melting from 72-73 degrees was obtained. The best yield obtained in a well closed trail was 40 per cent of the weight of acid used.

(2) One part of the acid was added to one part of methyl alcohol and dry hydrogen chloride was passed in until the solution was completely saturated. The solution was poured into water and filtered. The filtrate was extracted 12 times with ether, washed with a dilute solution of sodium carbonate

then dried with calcium chloride. The solution was evaporated and a brown sticky substance remained that could not be crystallized. Later it was concluded that if the mass were distilled under diminished pressure methyl coumalinate would be obtained.

(3) 10 grams of coumalinic acid was dissolved in ammonia water, made almost neutral with nitric acid and silver nitrate added. The silver salt was filtered off and placed into a flask connected to a reflux condenser. Ether and methyl iodide were added respectively and the solution was permitted to reflux for three hours. After evaporating the ether solution a brown mass remained which could not be crystallized.

(4) To 30 grams of coumalinic acid and 5 cc. sulphuric acid, 60 cc. of methyl alcohol was added. Absolute methyl alcohol vapors were passed through the mixture removing the water formed in the reaction. When the reaction was complete, the solution was cooled, poured into water and the oil layer was separated from the water layer. The water layer was extracted twelve times with ether, made neutral by washing with a dilute solution of sodium acid carbonate, dried with calcium chloride and the ether evaporated. The resulting material was distilled under diminished pressure. Methyl coumalinate distilled over between 170-180 degrees and 60 mm. Melting point of the ester, 73-74 degrees. The oil layer of distillation gave 6 grams of methyl coumalinate. Total yield of ester was 48 per cent of the weight of acid used.

Methyl-chlorocoumalinate

To 30 grams of pure methyl coumalinate (V), the calculated amount of carbon tetrachloride saturated with 7-8 per cent chlorine was added and allowed to stand at room temperature. After two or three days hydrogen chloride started to be given off and crystals formed. The crystals were separated, and washed with ether. The crude product (25 grams) was then recrystallized from alcohol. 17 grams of pure chloro-ester melting, 134-136 degrees was obtained.

This method was tried about a dozen times with 5 to 10 grams of pure methyl coumalinate and the best yield obtained was one gram of pure methyl-chlorocoumalinate for every 10 grams of methyl coumalinate. The crude product obtained melted between 94-103 degrees, but after recrystallizing three times from alcohol, a pure product melting, 133-135 degrees was secured.

Sulphuryl chloride was tried instead of carbon tetrachloride but the yield was not increased.

* Furane 2:4 dicarboxylic acid.

Methyl-bromocoumalinate (5grams) were mixed in a cold solution containing (10 grams) potassium hydroxide in (20 grams) of water. It was heated for twenty minutes, allowed to cool and then neutralized with sulphuric acid. The whole mass was placed on a water bath to dry. The brown mass remaining was extracted with acetone. After vaporizing the acetone a brown mass remained which was washed with ligroin and recrystallized from hot water. The yield was 3.7 grams, melting at 260 degrees.

When 2 grams of methyl-chlorocoumalinate was obtained, the procedure as given above was followed through. The brown mass obtained after vaporizing the acetone was insufficient to carry the operation any further. Lack of time prevented the preparation of more methyl-chlorocoumalinate; thus the problem had to be left without a definite conclusion.

CUSCUPY

Cuscupic acid was prepared in better yields than that recorded in the literature.

The acid was esterified using sulphuric acid as catalyst.

Difficulty was experienced in preparing ethyl-chloro-cuscupate in sufficient quantities to work with. One experiment, ethyl-chloro-cuscupate plus potassium hydroxide gave no solid product.

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